Comparative Thermal Stability of Homopolysiloxanes and Copolysiloxanes of Dimethyl/Diphenyl Silanes

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Summary:The thermal degradation study of homopolysiloxane and copolysiloxanes of dimethyl/diphenyl silanes have been carried out. The analysis of the degradation products by mass spectrometry, and infra-red spectroscopy show the presence of oligomers and benzene. The mechanism of degradation is discussed and it has been found that one copolysiloxane containing 75% methyl and 25% phenyl is the most stable among the series studies.

Introduction

Thermal degradation study of polysiloxanes is interesting as a variety of such materials are commercially exploited [1]. Previous investigation [2,3] of thermal degradation of polydimethylsiloxanes and polymethylphenylsiloxanes have demonstrated that the replacement of methyl by phenyl group in polydimethylsiloxane molecule results in enhanced stability. In this paper we report a comparison between thermal stabilities of a series of copolysiloxanes and hompolysiloxanes of dimethyl/diphenyl silane.

The homopolysiloxanes and copolysiloxanes which have been studied can be represented as proposed by Hurd [4]. The difunctional units dimethyl and diphenylsiloxanes are represented by D and D' respectively so that the copolysiloxane containing n units of D and D' would be represented as $D_n D'_n D_n$ etc. The number average molecular weight of the polysiloxanes fall in the range of 3000 to 10964. The polymers were purified from the monomers and oligomers under vacuum and by repeatedly dissolving and precipitating the polymers with suitable solvent. The polymers were capped with trimethylsilane before purification.

Experimental

Preparation of Homopolysiloxane

Polydimethylsiloxane and polydiphenylsiloxane were prepared by hydrolysis of the appropriate dichlorosilane.

One mole of respective dichlorosilane diluted with toluene was taken in a flask equipped with a reflux condenser and a dropping funnel. 2.00 mole of water and 1 ml. of conc. H_2SO_4 was introduced drop by drop with vigorous and constant stirring. The reaction mixturewas refluxed for eight hours. Toluene was evaporated off and siloxane formed was suspended in ether. The ether layer was washed several times with water, dried over anhydrous $MgSO_4$ and ether removed under vacuum, followed by termination of the chain by treating with trimethyl chlorosilane in toluene.

Preparation of Copolysiloxane

Copolymers of dimethyldichlorosilane and diphenyldichlorosilane were prepared by the cohydrolysis of respective monomers in 3:1, 1:1 and 1:3.

A mixture of dimethyldichlorosilane and diphenyldichlorosilane was taken in a flask fitted with reflux condenser and a droppingfunnel one ml of conc. H_2SO_4 was added and water was introduced drop by drop with vigorous stirring. The reaction mixture was refluxed for eight hours. The copolymer formed was washed with water, dried and isolated as described above in the case of homopolysiloxane.

Purification of Polysiloxanes

Homopolysiloxanes and copolysiloxanes were subjected to purification. For this purpose each polysiloxane was dissolved in diethyl ether, filtered and the volume of the polymer solution was reduced to appropriate concentration before precipitating the polysiloxane by dropping slowly into methanol. This process was repeated twice. The purified polysiloxane was filtered and dried under vacuum to remove the traces of solvents.

Gel Permeation Chromatographic Measurements

Molecular weights were measured using a Shimadzu LC-6A type high performance liquid chromatograph equipped with gel permeation chromatographic facilities. All values of molecular weight reported in this paper are give on the basis of calibration *via* elution volume obtained with standard polystyrene samples with narrow molecular weight distribution. The number average molecular weight values obtained by using ultra-violet (UV) detector, were compared with those obtained by the refractive index (RI) detector Table-1.

Table-1

Polymer	Monomer	Diphenyl monomer in feed(mole %)	Diphenyl units in co-polymer (mole %)	Mn UV Detector	RI Detector
A	D	0	-	2810	3310
B	DD'	25	27	10970	10960
C	DD'	50	52	6910	7070
D	DD'	75	76	4570	4570
E	D'	100	100	4780	4890

D = dimethyl silane D' = diphenyl silane

Degradation Technique

Programmed thermogravimetry was performed using 10 mg. samples at 10°C/min under dynamic nitrogen (70 ml/min) using a Du pont model 990 thermoanalyser.

For the examination of the degradation products, the 100 mg of the sample was degraded at 500°C in an evacuated twin limb glass tube. One end of the tube was placed in the oven while the other limb was placed in a liquid nitrogen trap to collect the degradation products for subsequent analysis. These volatilies were then subjected to analysis using a Kratus Ms 30 mass spectrometer.

Results and Discussion

Comparison of thermal stability and degradation mechanism of copolysiloxanes and homo-polysiloxanes is presented on the basis of experimental data obtained from TG/DTG, and mass spectra.

A typical NMR spectrum is shown in Fig. 1. The NMR absorptions due to phenyl and methyl
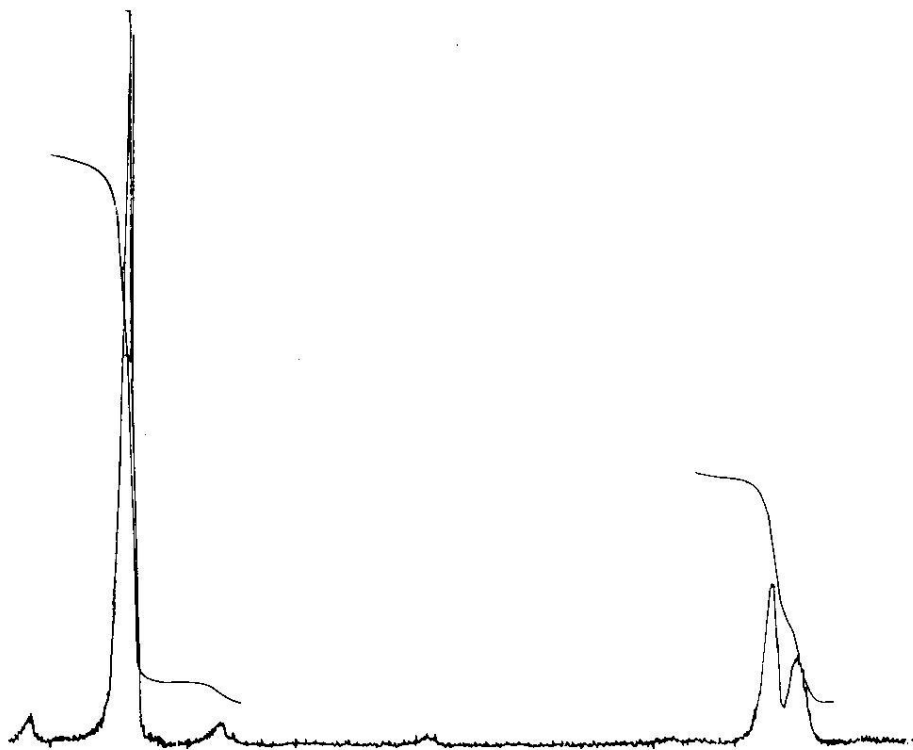

Fig.1: NMR spectrum of polysiloxane D.

groups around 7 ppm and 1 ppm respectively have been used to determine the phenyl/methyl ratios of the copolymers (Table-1). The table indicates the mole % of diphenyl contents in all copolymers are higher than mole % of diphenyl in the monomer feed. This indicates the higher reactivity of the diphenyl monomer as compared to dimethyl monomer.

TG/DTG curves of the trimethylsiloxy terminated homo and copolysiloxanes are shown in Fig. 2(a,b). The curves demonstrate that amount of residue initially decreases with increase in diphenyl blocks in polymer chains and the homopolysiloxane
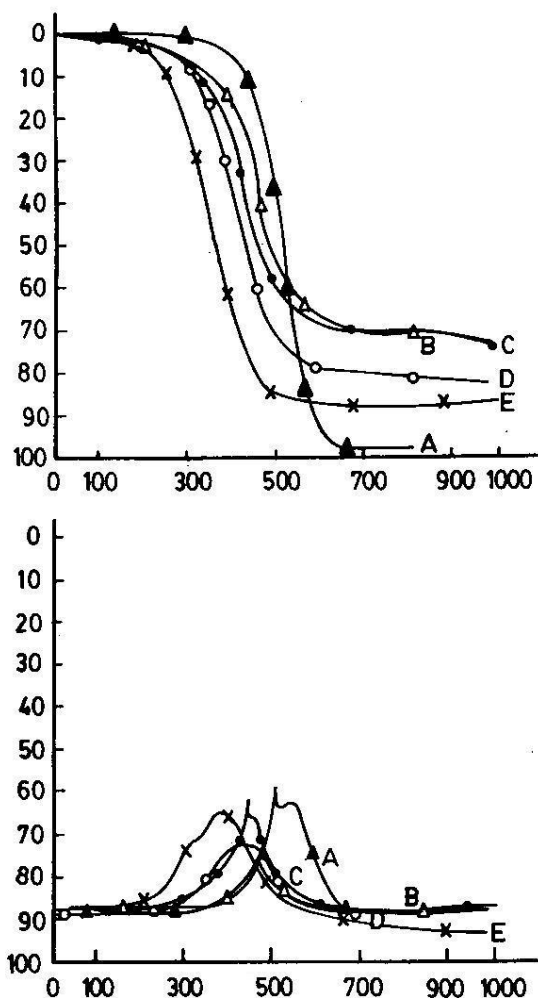
Fig. 2: (a,b) TG/DTG curves of various trimethylsiloxy terminated homo and copolysiloxanes (dynamic nitrogen, 10°C/min).

(sample E) containing 100% diphenyl units has a minimum residue of 15%. The degradation of various polysiloxanes takes place in the temperature range of 300 to 350°C.

Mass spectra of degradation products for various polysiloxanes are shown in Table-2. It can be seen that most of the degradation products are linear and cyclic oligomers and in case of copolysiloxane, benzene is also a co-product.

With respect to the main depolymerization reaction any mechanism for the production of cyclics from the polysiloxanes inevitably requires a degree of mobility for the polymer chain. The mechanism proposed [5] is most straight forward representation for the formation of cyclics.
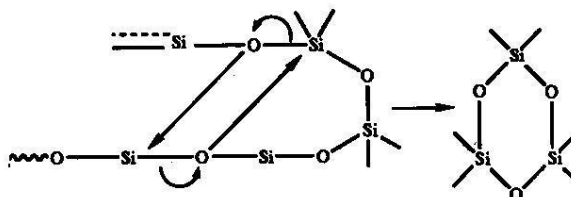
This reaction will be inhibited with increasing structurization of the polymer. The mobility of a polymer capped with trimethylsiloxy units will not be hindered in this manner and under favourable conditions such a polymer can therefore degrade to completion.

At higher temperatures copolysiloxanes degrade to yield more benzene than can be accounted for by involvement of chain ends alone. Clearly the Si-Ph bond is being cleaved in a more random process. This process should primarily be independent of the initial molecular weight of the polymer. The other factors such as diffusion and chain mobility are often important in determing the course of reactions of this nature and it is reasonable that at any given temperature the reaction might proceed until such secondary factors prohibit it.

An altrnative free radical mechanism might be considered.
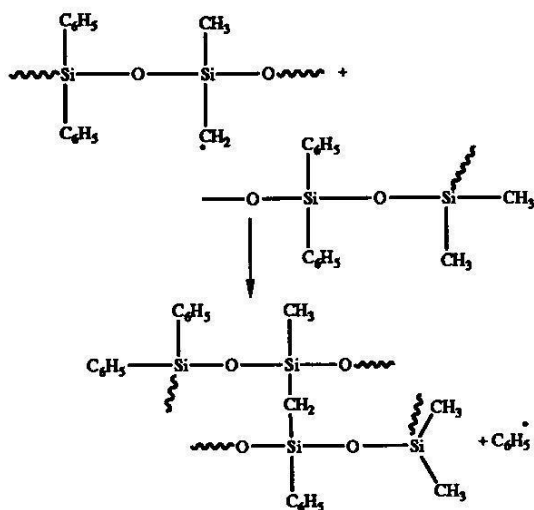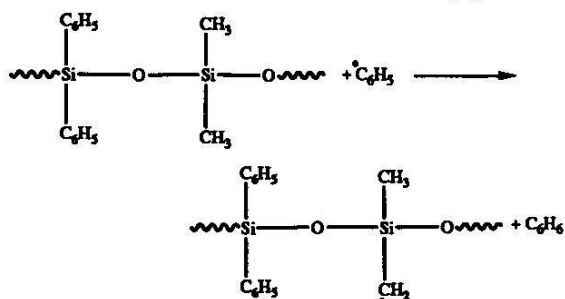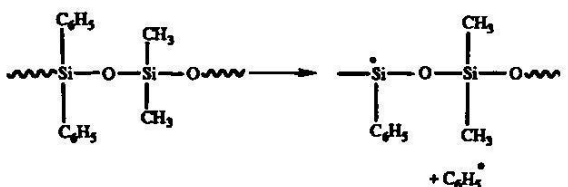
The generation of polysiloxane containg -CH2- group is supported by the mass spectral studies. Further degradation of such polysiloxane can be explained as follows:
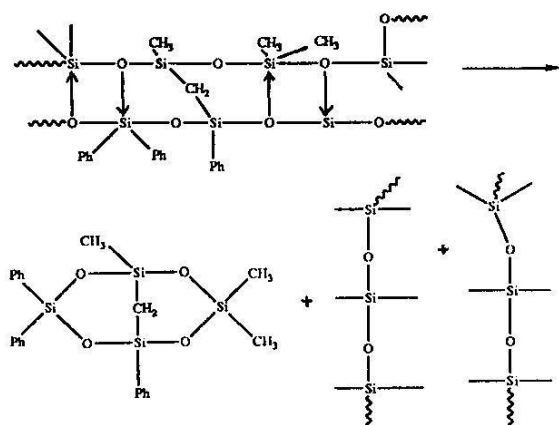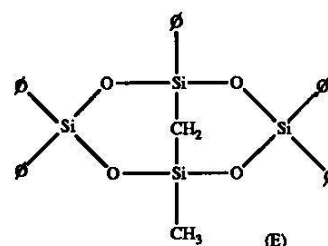

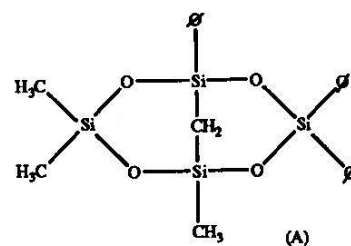Table-2: Mass Spectrum Analysis of Various Degradation Products of Polysiloxanes

Poly-mer	m/z	Relative Abun-dance	Proposed Structure
A	i) 429 (M-15)	22.1	D6
	ii) 355 (M-15)	94.0	D5
	iii) 281 (M-15)	15.0	D4
	iv) 207 (M-15)	100.0	D3
	v) 133 (281-148)		
	vi) 73		Si(CH3)3
	vii) 59 (207-148)		
B	544(M)	2.2	D2D2' (Ph4Me4Si4O4)
	529 (M-15)	4.4	(D2D2' - 15)
	466	8.1	

	451 (A-15)	11.7	(A-15)
	420 (M)	1.8	D3D1' (B)
	405 (B-15)	21.0	D3D1'
	346 (M)	6.3	D2D1' (C)
	331 (C-15)	15.7	D2D1'
	281(M-15)	2.9	D4
	207 (M-15)	4.9	D3
	198 ((M-1)	6.8	(C6H5)2SiO
	197 (M-1)	36.8	(C6H5)2 SiO-1
	135	100.0	
	73	57.8	Si(CH3)+
C	i) 590	16.9	

	ii) 575 (E-15)	7.2	
	iii) 544 (M)	11.2	D2D2'
	iv) 529 (M-15)	27.4	D2D2'
	v) 513 (E-77)	16.7	E
	vi) 470	31.3	D1D2'
	466	9.2	A
	455 (D1D2'-15)	22.6	D1D2'
	451 (A-15)	45.8	A
	405 (D3D1-15)	5.5	D3D1'
	377	72.0	
	331 (D2D1'-15)	8.0	D2D1'
	198	19.0	(C6H5)2SiO

Table-2: continued.

Poly-mer	m/z	Relative Abundance	Proposed Structure
	197	99.3	$(C_6H_5)_2SiO$
	135	100.0	
	73	26.2	$Si(CH_3)_{3+}$
D	594 (M)	13.3	D_3'
	590	10	
	575 (E-15)	12	E
	544 (M)	17.9	D_2D_2'
	529 (M-15)	41.4	D_2D_2'
	513 (E-77)	21.5	E
	470 (M)	34.3	D_1D_2'
	455 (M-15)	24.4	D_1D_2'
	451 (A-15)	55.6	A
	377	71.7	-
	346	2.3	D_2D_1'
	331 (C-15)	7.3	D_2D_1
	198 (M)	18.6	$(C_6H_5)_2Si\,O$
	197 (M-1)	100	$(C_6H_5)_5\,Si\,0\text{-}1$
	197	17.3	$(C_6H_5)_2$
	154	66.2	
	135		

Mass spectra of this species is consistent with the structures drawn above. Clearly, a number of alternative structure can be drawn consistent with the

MS of the degradation products of copolymers B,C,D by more than one rearrangements of above atoms and groups of atoms. However such rearrangement will not be straight forward. The major products of degradation of polymethyldiphenylsiloxane are cyclic trimers and cyclic tetramers. Different isomers of cyclic trimer and tetramer can be drawn which are consistant with recorded mass spectra (Table-2).

References

1. W.Noll. Chemistry and Technology of Silicones Academic Press. 531, (1968).
2. N.Grassie and K.F. Francey, *Polymer degradation and stability*, 2, 53 (1980).
3. N. Grassie, K.F. Francey, I.G. Macfarlane *Polymer degradation and stability*, 2, 67 (1980).
4. C.B. Hurd, *J.Am.Chem.Soc.*, 68, 364 (1946).
5. N.Grassie, G. Scott, Thermal Degradation, Polydegradation and Stabilization, ed. N. Grassie and G.Scott, Cambridge University Press London, pp. 35 (1985).